



## Electrocatalytic activity of platinum modified polypyrrole films for the methanol oxidation reaction

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### Abstract

The catalytic activity of platinum modified polypyrrole films prepared in different ways was studied for the methanol oxidation reaction. Surprisingly, no catalytic activity was observed for films modified with colloidal platinum particles incorporated into the film during its synthesis or for the film synthesised with tetrachloroplatinate complex as a nucleophilic counter-ion, which was subsequently cathodically reduced. On the other hand, high catalytic activity was observed for platinum deposited onto pre-synthesised polypyrrole film. The platinum load, film thickness and potential of platinum deposition were found to be important parameters. High electrocatalytic activity was also observed for platinum layers deposited directly onto the glassy carbon (GC) support. However, in the latter case the stability of the electrocatalytic activity was lower when compared with the polypyrrole film modified by cathodically deposited Pt.

### 1. Introduction

The application of conducting polymers as support for platinum catalyst particles for the anodic oxidation of hydrogen or small organic molecules has been the subject of numerous investigations [1–13]. The main reason for studying such composite material is the extraordinary electrocatalytic activity, which is comparable with or even exceeding that of bare platinum at relatively low Pt load. In the case of polyaniline (Pani), Lamy et al. [12] reported that  $0.15 \text{ mg cm}^{-2}$  of Pt are sufficient to obtain catalytic activities comparable to that of bare Pt for the hydrogen oxidation reaction. In our previous work, using polypyrrole (PPy) as catalyst support, Pt loads between 0.2 and  $0.5 \text{ mg cm}^{-2}$  were necessary to achieve comparable efficiencies, depending on the method of Pt deposition [14]. This difference may be explained by the approximately 20 times larger thickness of the supporting PPy film used in our studies.

Another reason for using conducting polymers as support for the platinum catalyst is the reportedly higher tolerance of the Pt microparticles to CO. This effect is not yet understood. It was shown by Lamy et al. [10] that Pt particles deposited onto Pani are covered to a much lower extent by strongly adsorbed CO species as compared with the bare Pt electrode. Several explana-

tions of this phenomenon have been proposed, e.g., the formation of strongly adsorbed species is less probable on Pt microparticles [15] or the interaction of the Pt microparticles with the conducting polymer matrix reduces the formation of strongly chemisorbed species [8]. Aramata and Ohnishi [16] studied the catalytic activity of Pt particles dispersed inside a cation-exchanger membrane. The increased resistivity against catalyst poisoning was explained in terms of stabilising a  $\text{Pt}^0/\text{Pt}^{2+}$  surface mediator couple which regenerates the electrocatalytic active sites.

Pani is the most common conducting polymer used as support for the Pt microparticles forming a composite catalyst for the methanol oxidation reaction, whereas only two papers dealing with a PPy–Pt composite catalyst have been found in the literature for this reaction [9, 13]. In our previous paper we applied different methods to modify PPy with Pt to provide an homogeneous Pt distribution over the whole cross-section of the catalyst film and tested the electrocatalytic activity for the hydrogen oxidation reaction [14].

The aim of the present work was to study the methanol oxidation reaction on the different PPy/Pt composite materials and to characterise their catalytic activity by different means.

### 2. Experimental

Electrochemical measurements were performed with a potentiostat–galvanostat (HEKA PG310) using a

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double-compartment glass cell with standard three-electrode configuration. All potentials in the text refer to the SCE.

All chemicals used were commercial materials of the highest purity. In all cases PPy was synthesised potentiostatically at 0.75 V. The temperature was kept constant at 20 °C. The thickness of the film was controlled by the anodic charge flowing during the anodic polarisation. An amount of 100 mC cm<sup>-2</sup> was considered to correspond to a film thickness of 0.25 µm [11, 14, 17]. A glassy carbon (GC) rotating disk electrode (RDE) served as substrate for the composite catalyst film.

As previously described [14], samples denoted as Pt/PPy(I) were prepared by cathodic deposition of Pt onto a pre-synthesised PPy film obtained from 0.1 M Pyrrole(Py) + 0.1 M NaCl solution. Platinum was deposited potentiostatically from 1 mM H<sub>2</sub>PtCl<sub>6</sub> + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

Samples denoted as Pt/PPy(II) were prepared by polymerisation of the PPy film from colloidal solutions of nano-scale Pt particles according to the procedure described by Bose and Rajeshwar [18]. The required amount of H<sub>2</sub>PtCl<sub>6</sub> was added to 6.5 cm<sup>3</sup> sodium hydrogen citrate solution. To avoid the bulk polymerisation of PPy, citrate was present in the 3 and 0.4 mM H<sub>2</sub>PtCl<sub>6</sub> plating solutions at concentrations of 11.5 and 1.9 mM, respectively. The final plating baths were prepared from 10 cm<sup>3</sup> of these solutions, after treatment in an ultrasonic bath for 7 min, by adding 1 cm<sup>3</sup> of 1 M NaCl solution and 2.5 cm<sup>3</sup> of 0.2 M Py solution.

Samples denoted as Pt/PPy(III) were prepared by electropolymerisation of PPy from a solution of 0.05 M pyrrole and 10 mM K<sub>2</sub>PtCl<sub>4</sub>. After the electropolymerisation the samples were cycled 40 times between +0.6 and -0.6 V in 0.5 M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 50 mV s<sup>-1</sup> to reduce the tetrachloroplatinate incorporated as counter ion in the PPy film. Further details about synthesis and modification of the PPy film are given elsewhere [14].

Scanning electron microscopy (SEM) was used for the elemental analysis of the samples (Philips microscope type XL-40 with EDX option from EDAX). Metallic Pt particles were observed for the Pt/PPy(I) sample only. The size of the crystallites varied in the range 0.1–0.4 µm depending on the particular Pt load.

The catalytic activity of the Pt/PPy composite film was tested by methanol oxidation in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M methanol solution. All experiments were carried out under N<sub>2</sub> atmosphere and the temperature was kept constant at 25 ± 0.1 °C.

### 3. Results

Figure 1 shows the cyclic voltammogram of the bare Pt electrode in acidic methanol solution. The polarisation curve is in good agreement with those obtained by Lamy et al. [15]. Slight hysteresis in the peak potential range is usually attributed to blocking of surface sites by

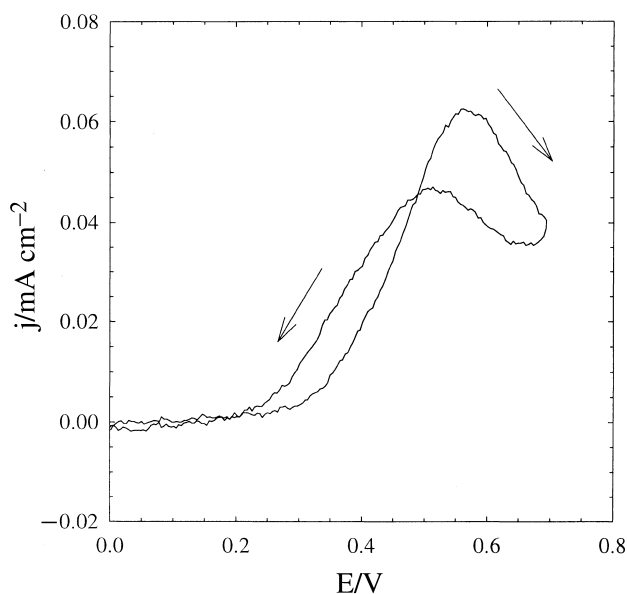


Fig. 1. Cyclic voltammogram of the rotating disk bare Pt electrode in 1 M MeOH in 0.5 M H<sub>2</sub>SO<sub>4</sub> under N<sub>2</sub> atmosphere at 25 °C, potential scan rate 5 mV s<sup>-1</sup>, rotation rate 1000 RPM.

strongly chemisorbed CO intermediates [17]. These species are oxidised at more anodic potentials to CO<sub>2</sub> thus reactivating the surface for the oxidation of methanol in the cathodic sweep. This phenomenon is not so pronounced in the voltammogram of Figure 1, since the anodic vertex potential was relatively low.

#### 3.1. Electrocatalytic activity of the Pt/PPy(II) composite catalyst

As a first step, the catalytic activity of the samples with a regular Pt distribution over the film cross-section was tested. The cyclic voltammograms of the Pt/PPy(II) composite in acidic MeOH solution are shown in Figure 2. Surprisingly, enhanced electrocatalytic activity was not observed for the composite catalyst. Moreover, the sample exhibits even inhibition of the oxidation/reduction processes of PPy, probably caused by its interaction with MeOH. Various concentrations of PtCl<sub>6</sub><sup>2-</sup> in the synthesis solution were tested, ranging from 0.4 to 3.0 mM. Reduced film thickness (0.5 µm) and polyanion (polystyrene sulphonate) as a nucleophilic counter-ion were used to identify the possible influence of these parameters on the electrocatalytic activity of these composite films. However, an anodic peak, corresponding to MeOH oxidation, could not be observed for any of these samples.

#### 3.2. Electrocatalytic activity of the Pt/PPy(III) composite catalyst

The cyclic voltammograms of the Pt/PPy(III) composite catalyst in sulphuric acid solution with and without MeOH are shown in Figure 3. Also in this case an electrocatalytic activity for the MeOH oxidation reaction could not be observed and the redox processes of

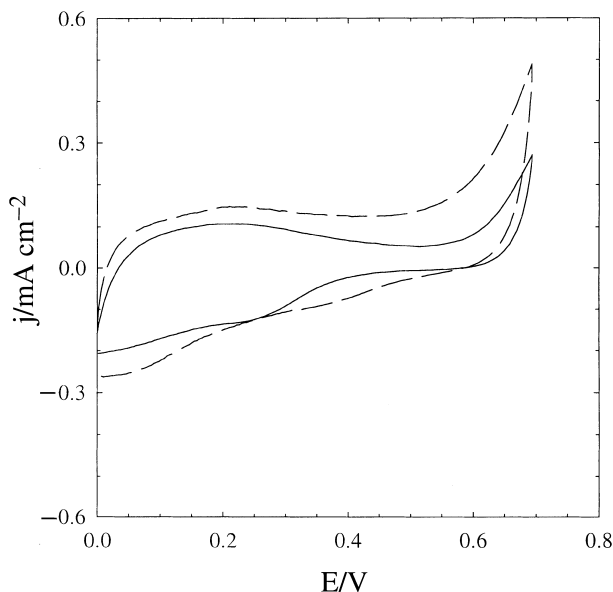


Fig. 2. Cyclic voltammogram of the rotating GC disk electrode covered with Pt/PPy(II) composite 1  $\mu\text{m}$  thick in 0.5 M  $\text{H}_2\text{SO}_4$  under  $\text{N}_2$  atmosphere at 25  $^\circ\text{C}$ , concentration of  $\text{PtCl}_6^{2-}$  in the synthesis solution 1.8 mM, potential scan rate 5  $\text{mV s}^{-1}$ , rotation rate 1000 RPM; electrolyte (—) with 1 M MeOH, (---) without MeOH.

the composite film were also inhibited. As observed in our previous study on hydrogen oxidation [14], the catalytic activity increases with decreasing Pt/PPy(III) film thickness. But reduction in the film thickness down to 0.1  $\mu\text{m}$  was not effective to obtain a remarkable electrocatalytic activity for the MeOH oxidation reaction.

### 3.3. Electrocatalytic activity of the Pt/PPy(I) composite catalyst

The method of PPy film modification by the cathodic deposition of Pt on a pre-synthesised conducting polymer film was tested. Cyclic voltammograms of samples with different loads of Pt deposited potentiostatically on a pre-synthesised PPy film of 10  $\mu\text{m}$  thickness are shown in Figure 4. For the lowest Pt load of 0.5  $\text{mg cm}^{-2}$  no electrocatalytic activity is apparent. This changes when the Pt load is increased up to 0.9  $\text{mg cm}^{-2}$ . An anodic shoulder, corresponding to MeOH oxidation, appears on the polarisation curve. However, the Pt load needed to observe this positive catalytic effect is higher than that reported by Strike et al. [9]. The reason is obviously the difference in the thickness of the polymer film. Therefore, a series of experiments was performed employing PPy films of 0.5  $\mu\text{m}$  thickness as support for the deposition of Pt microparticles. The results of various Pt loads are shown in Figure 5.

Three main phenomena can be observed in the polarisation curves of MeOH oxidation. Firstly, an anodic shoulder appears in the curves of the three lowest Pt loads, partly overlapped by an anodic peak. The origin of this peak is not clear so far. It seems to be connected with the interaction of PPy and MeOH, or

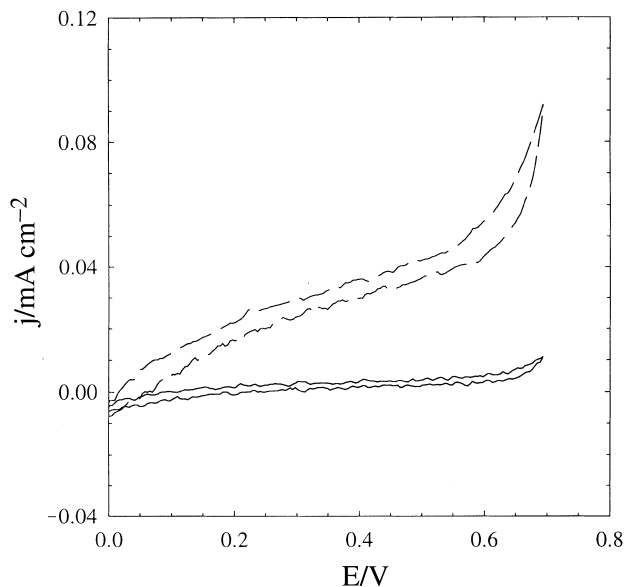


Fig. 3. Cyclic voltammogram of the rotating GC disk electrode covered with Pt/PPy(III) composite 0.5  $\mu\text{m}$  thick in 0.5 M  $\text{H}_2\text{SO}_4$  under  $\text{N}_2$  atmosphere at 25  $^\circ\text{C}$ , concentration of  $\text{PtCl}_4^{2-}$  in the synthesis solution 10 mM, potential scan rate 5  $\text{mV s}^{-1}$ , rotation rate 1000 RPM; electrolyte (—) with 1 M MeOH, (---) without MeOH.

PPy, Pt and MeOH. This follows from the fact that the peak does not appear in electrolyte solution without MeOH and with GC electrodes modified with cathodically deposited Pt only. The peak potential corresponds to the overoxidation of PPy, but it is not observed in absence of MeOH. It is interesting to note that the current density of this peak increases strongly with

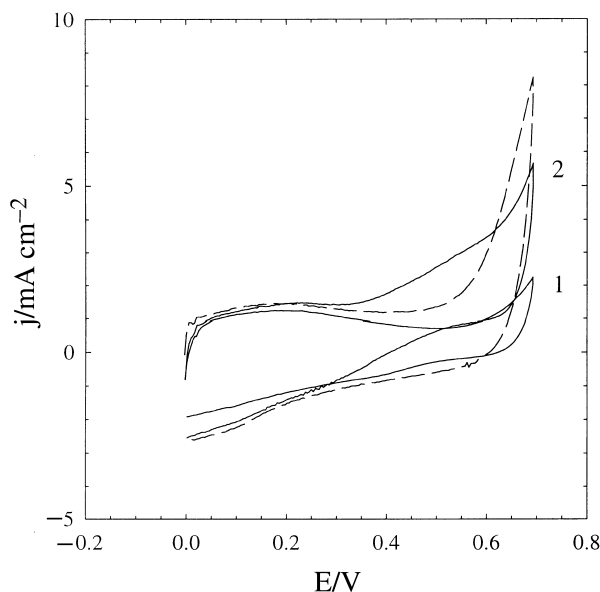


Fig. 4. Cyclic voltammogram of the rotating GC disk electrode covered with Pt/PPy(I) composite 10  $\mu\text{m}$  thick in 0.5 M  $\text{H}_2\text{SO}_4$  under  $\text{N}_2$  atmosphere at 25  $^\circ\text{C}$ , Pt deposition potential  $E = +0.2 \text{ V}$ , potential scan rate 5  $\text{mV s}^{-1}$ , rotation rate 1000 RPM; electrolyte (—) with 1 M MeOH, (---) without MeOH; curve was obtained for following Pt load (in  $\text{mg cm}^{-2}$ ): 1–0.5 and 2–0.9.

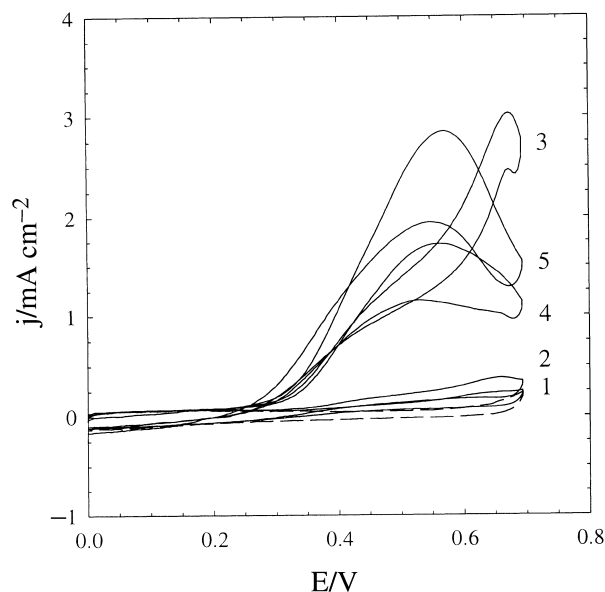


Fig. 5. Cyclic voltammetric curve of the rotating GC disk electrode covered with Pt/PPy(I) composite  $0.5 \mu\text{m}$  thick in  $0.5 \text{ M H}_2\text{SO}_4$  under  $\text{N}_2$  atmosphere at  $25^\circ\text{C}$ , Pt deposition potential  $E = +0.2 \text{ V}$ , potential scan rate  $5 \text{ mV s}^{-1}$ , rotation rate  $1000 \text{ RPM}$ ; electrolyte (—) with  $1 \text{ M MeOH}$ , (---) without MeOH; curve was obtained for following Pt load (in  $\text{mg cm}^{-2}$ ): 1–0.2, 2–0.3, 3–0.5, 4–0.6 and 5–0.9.

increasing Pt load. This indicates the catalytic influence of Pt on the related electrochemical process.

Secondly, when the Pt load exceeded a certain amount ( $0.5\text{--}0.6 \text{ mg cm}^{-2}$ ), this anodic current peak disappears. This may be explained by the fact, that at high Pt loads, the deposited Pt islands merge into a compact Pt layer covering the PPy film surface. Such composites show a behaviour qualitatively similar to that of the bare Pt electrode (Figure 1) and the Pt layer protects the underlying PPy film from interaction with MeOH.

Thirdly, for both types of voltammetric curves, the hysteresis typical for bare Pt was also observed. This indicates that chemisorption of reaction intermediates on the Pt surface still proceeds, which may gradually differ in the degree of coverage and the strength of adsorption, as will be discussed later.

As discussed previously [14], the potential of Pt deposition is another crucial parameter in the catalyst formation process. In order to test this influence on the catalytic activity of MeOH oxidation, different amounts of Pt were deposited onto pre-synthesised PPy film at  $-0.1 \text{ V}$  instead of  $+0.2 \text{ V}$ . The cyclic voltammograms obtained for the different Pt loads are shown in Figure 6. The current density of the anodic peak differs substantially from that of the samples prepared at  $+0.2 \text{ V}$ . Obviously, at the more cathodic deposition potential,  $E = -0.1 \text{ V}$ , the Pt forms a less compact open structure. Such a layer does not shield the underlying PPy film from MeOH interaction and promotes the process related with the overlapping anodic peak. The current density corresponding to MeOH oxidation is also much higher in comparison to that of the samples modified at  $+0.2 \text{ V}$ .

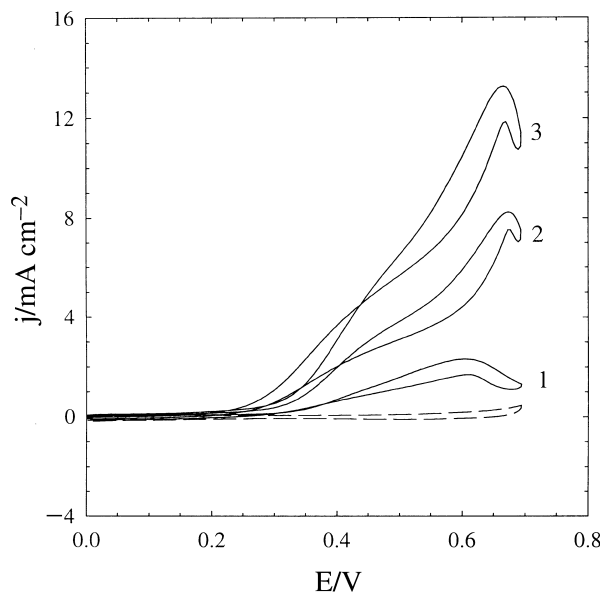


Fig. 6. Cyclic voltammetric curve of the rotating GC disk electrode covered with Pt/PPy(I) composite  $0.5 \mu\text{m}$  thick in  $0.5 \text{ M H}_2\text{SO}_4$  under  $\text{N}_2$  atmosphere at  $25^\circ\text{C}$ , Pt deposition potential  $E = -0.1 \text{ V}$ , potential scan rate  $5 \text{ mV s}^{-1}$ , rotation rate  $1000 \text{ RPM}$ ; electrolyte (—) with  $1 \text{ M MeOH}$ , (---) without MeOH; curve was obtained for following Pt load (in  $\text{mg cm}^{-2}$ ): 1–0.2, 2–0.4 and 3–0.5.

### 3.4. Electrocatalytic activity of GC modified by cathodically deposited Pt

The negative influence of increasing polymer film thickness on the electrocatalytic activity of the composite catalyst provoked the idea to test the behaviour of a Pt layer deposited directly onto the GC electrode surface. Cyclic voltammograms of GC electrodes modified with different Pt loads are shown in Figure 7. It can be seen that the catalytic activity for the MeOH oxidation reaction is higher than that of the Pt covered PPy film at a comparable Pt load.

## 4. Discussion

An important result of the present work is the finding that the composites of PPy with three-dimensional distribution of Pt, i.e. Pt/PPy(II) and Pt/PPy(III), does not exhibit catalytic activity for the MeOH oxidation reaction.

With regard to the Pt/PPy(II) catalyst it can be assumed that this is due to low Pt surface concentration. As shown in [14], the concentration of Pt over the film cross-section apparently decreases near the film surface. Additionally, only a part of the Pt indicated by EDX is probably present in the reduced form. This results in a very low or negligible electrocatalytic activity for MeOH oxidation. The absence of catalytic activity of the Pt/PPy(III) composite, is surprising, because in this particular case the total Pt concentration in the film was very high [14]. This confirms that the concentration of Pt in the polymer film is of secondary importance. More

important seems to be the form of the Pt present inside the film. In the case of the Pt/PPy(II) composite it was concluded that at least part of the Pt is present in the form of a Pt chloro-complex inside the film structure [14], which is catalytically not active for the MeOH oxidation reaction.

Similarly, there is also no direct evidence that in the Pt/PPy(III) composite Pt is present only in the reduced state. Using transmission electron microscopy, Hepel [13] has shown that Pt exists inside the PPy film in the form of metallic nanoparticles. However, the detailed analysis indicating to what extent the Pt chloro-complex is reduced by subsequent potential cycling after synthesis of the film has not been provided so far. The question of electroneutrality within the film during reduction of the incorporated chloroplatinate and its influence on the kinetics of the reduction process was discussed in [14]. Hepel et al. [19] concluded from the results of electrochemical quartz crystal microbalance (EQCM) measurements that  $\text{PtCl}_4^{2-}$  is reduced to metallic Pt. However the mass changes observed can also be explained in terms of slow ion exchange processes during the dynamic polar-

isation of the film, since the authors also reported a loss of the PPy-like characteristics after potential cycling of the composite film [13, 19]. The same phenomenon was observed in our previous work [14].

Another explanation for the absence of the electrocatalytic activity of Pt/PPy(III) composites may be related to the cathodic vertex potential of the cyclic voltammetric reduction of tetrachloroplatinate complex in the film, as already discussed in [14]. According to our experimental conditions, the degree of chloroplatinate reduction to metallic platinum is expected to be relatively low.

Due to these considerations, the amount of metallic Pt present in the Pt/PPy(II) and Pt/PPy(III) composite systems is not exactly predicted and presumable rather low. As was shown for the Pt/PPy(I) composite, the amount of metallic Pt is of major importance for remarkable electrocatalytic activity.

Figure 8 shows the dependence of the peak current density  $j_p$  vs Pt load for methanol oxidation on PPy and GC with Pt deposited. For the three lowest Pt loads on PPy the current density at 0.5 V, i.e. in the middle of the current plateau, was taken for this plot. These values were corrected for the current density corresponding to the following anodic reaction (back ground current subtraction). For the remaining two highest Pt loads on PPy (deposited at  $E = +0.2$  V) the peak current density was not corrected as was the case for the Pt/GC system.

The plots in Figure 8 show that the activity of the electrocatalyst increases linearly with the amount of platinum deposited independent of the particular system. On the GC electrode approximately half the Pt load is sufficient to reach the activity of the correspond-

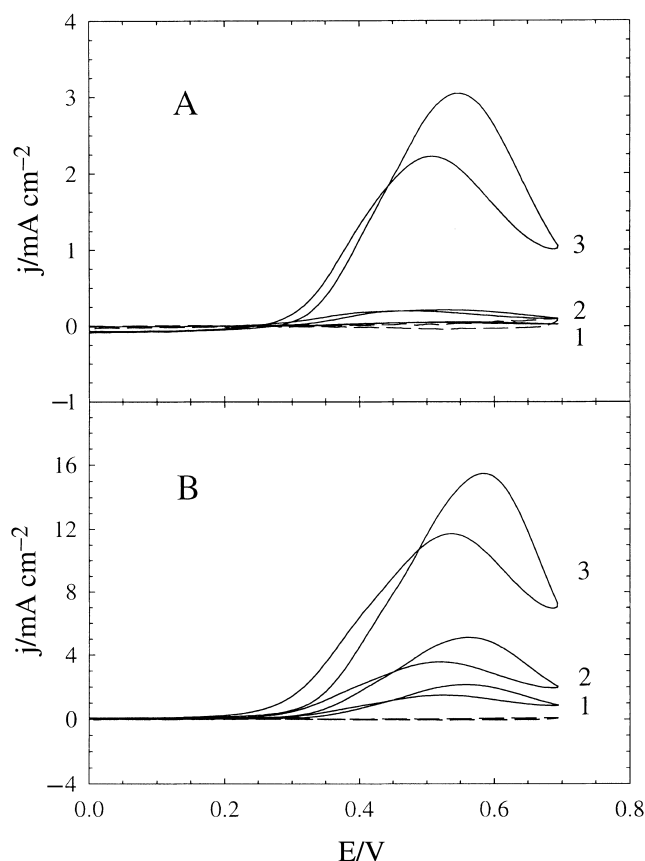


Fig. 7. Cyclic voltammetric curve of the rotating GC disk electrode covered with potentiostatically deposited Pt in 0.5 M  $\text{H}_2\text{SO}_4$  under  $\text{N}_2$  atmosphere at 25 °C, potential scan rate 5  $\text{mV s}^{-1}$ , rotation rate 1000 RPM; electrolyte (—) with 1 M MeOH, (---) without MeOH; (A) Pt deposition potential:  $E = +0.2$  V, curve was obtained for following Pt load (in  $\text{mg cm}^{-2}$ ): 1–0.02, 2–0.2 and 3–0.4; (B) Pt deposition potential:  $E = -0.1$  V, curve was obtained for following Pt load (in  $\text{mg cm}^{-2}$ ): 1–0.2, 2–0.4 and 3–0.5.

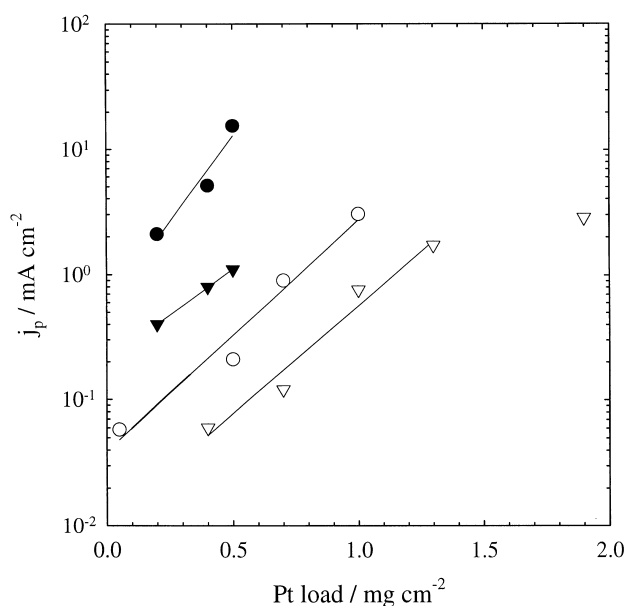


Fig. 8. Dependence of the MeOH oxidation peak current density on the potentiostatically deposited Pt load, 1 M MeOH in 0.5 M  $\text{H}_2\text{SO}_4$  under  $\text{N}_2$  atmosphere at 25 °C, potential scan rate 5  $\text{mV s}^{-1}$ , rotation rate 1000 RPM; electrode: (O) GC/Pt and ( $\nabla$ ) 0.5  $\mu\text{m}$  PPy/Pt, Pt deposition potential: (open symbols)  $E = +0.2$  V, (filled symbols)  $E = -0.1$  V.

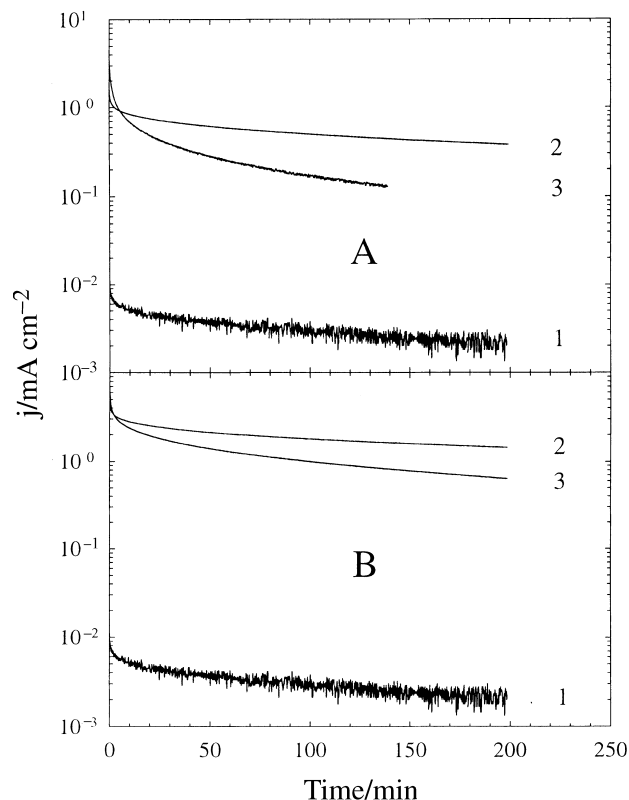


Fig. 9. Variation of the MeOH oxidation current density as a function of time at the potential of  $E = 0.5$  V, 1 M MeOH in 0.5 M  $H_2SO_4$  under  $N_2$  atmosphere at 25 °C, rotation rate 100 RPM; Pt load for GC/PPy/Pt and GC/PPy/Pt electrodes:  $0.4 \text{ mg cm}^{-2}$ ; Pt deposition potential: (A)  $E = +0.2$  V, (B)  $E = -0.1$  V.

ing Pt/PPy(I) composite electrode with  $0.5 \mu\text{m}$  PPy film thickness. Even more pronounced is this effect for electrodes modified by Pt at a potential of  $-0.1$  V. This raises the question of effectiveness of PPy as support for the Pt microparticles. Besides of the current density, i.e. the reaction rate, the time stability, i.e. the resistance against poisoning, is the most important parameter of the catalyst quality. It is evident from Figure 9 that, despite of the initially lower current density, the Pt/PPy(I) composite exhibits higher catalytic activity. After only 2 h of electrolysis the current density on Pt/PPy(I) electrode is well above that of the GC/Pt electrode independent of two different deposition potentials studied.

A possible explanation for the high current densities on GC/Pt can probably be found in the real surface area of the Pt particles accessible to MeOH oxidation. As shown in Figure 10, the Pt particles deposited on GC exhibit a spherical shape with a diameter of  $1\text{--}2 \mu\text{m}$ . Their size is almost half an order of magnitude larger than that of the Pt particles on the Pt/PPy(I) surface. To account for the high electrocatalytical activity, the concentration of active sites on the GC/Pt particles must be higher than on Pt/PPy(I). Another explanation would be a difference in the surface/Pt atoms co-ordination or catalyst–GC synergism. According to Mukerjee [20] such phenomena

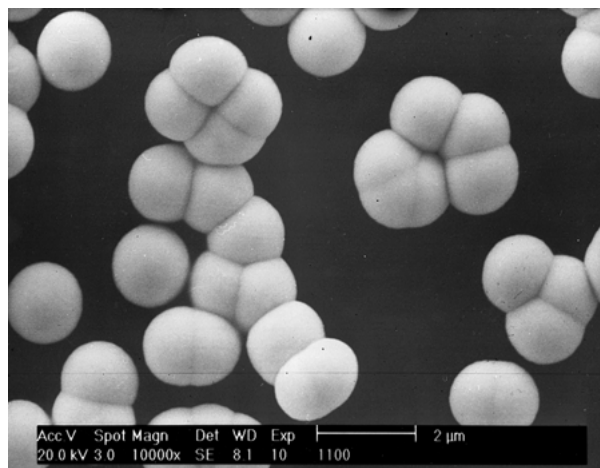


Fig. 10. SEM of the Pt cathodically deposited on the GC surface, Pt deposition potential  $E = +0.2$  V, Pt load  $0.3 \text{ mg cm}^{-2}$ .

come into play when the particle diameter is in the order of nanometers. In the case of Pt/PPy(I), the surface atoms of the Pt microparticles are partially shielded by the PPy matrix. On the another hand, the contact between Pt and PPy leads to enhanced stability of the catalytic activity, as documented in Figure 9.

Different surface area and number of active sites of deposited Pt particles may also explain the difference in the catalytic activity observed for the composite electrodes with Pt deposition at  $+0.2$  and  $-0.1$  V. Deposition at higher overvoltage results in the formation of deposits with a higher defect concentrations at the surface and an increase of real surface area thus providing an increase of the apparent current density.

## 5. Conclusion

The electrocatalytic activity of Pt/PPy composite electrodes prepared in different ways was tested for the methanol oxidation reaction. Using cyclic voltammetry, catalytic activity for the methanol oxidation was only found when the Pt particles were deposited on a pre-synthesised PPy film. The other types of composite films studied did not show sufficient catalytic activity for the oxidation of methanol. This could mainly be referred to the actual amount of metallic Pt present on the film surface.

High catalytic activity was also observed for Pt particles cathodically deposited on GC. However, the stability of the catalytic activity of the Pt modified PPy films was found to be better than that of the GC/Pt electrodes. This supports the idea of inhibiting CO poisoning by the interaction of Pt microparticles with the PPy support.

The potential of the cathodic Pt deposition on GC as well as on pre-synthesised PPy films was also found to be an important parameter for the electrocatalytic activity of composite electrodes.

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